IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): S. WU *et al.*

Attorney Docket No: 20002.0350

Application No.: 10/661,516

Group Art Unit: 3711

Filed: September 15, 2003

Examiner: A. Hunter

For: REACTION INJECTION MOLDABLE COMPOSITIONS, METHODS FOR MAKING SAME, AND RESULTANT GOLF ARTICLES

DECLARATION OF INVENTORS UNDER 37 CFR § 1.131

Commissioner for Patents
Washington, D.C. 20231

Sir:

We, Shenshen WU, Murali RAJAGOPALAN, Manjari KUNTIMADDI, and Kevin M. HARRIS hereby declare that:

1. Shenshen WU is a citizen of the United States and resides at 31 Cortland Grove Drive, Shrewsbury, MA 01545; Murali RAJAGOPALAN is a citizen of the United States and resides at 11 Flagship Drive, South Dartmouth, MA 02748; Manjari KUNTIMADDI is a citizen of India, and resides at 382 Finch Road, Raynham, MA 02767; and Kevin M. HARRIS is a citizen of the United States and resides at 65 Ryan Street, New Bedford, MA 02740.

2. That we are co-inventors of the invention disclosed and claimed in the above-identified patent application.

3. That, at the time of invention, we were employed by ACUSHNET COMPANY (formerly doing business as Titleist and Foot-joy Worldwide), 333 Bridge Street, Fairhaven, MA 02719, the Assignee of record of the entire, right, title and interest in the invention. Murali RAJAGOPALAN, Manjari KUNTIMADDI, and Kevin M. HARRIS are currently employed by ACUSHNET COMPANY.

4. That this declaration is filed to show that prior to October 1, 1999, we conceived and reduced to practice the subject matter of the claimed invention.

5. That attached hereto is Exhibit A. Exhibit A is a copy of the invention record for the present invention demonstrating conception and reduction to practice the claimed invention. For example, the process described in the invention record uses low viscosity materials for component A, *i.e.*, isocyanates, quasi-prepolymers, and prepolymers having a viscosity range from 25 cps to 2,000 cps (page 5). In addition, component B can be polyols and polyamines having a viscosity range from 25 cps to 2,000 cps (page 5), as well as epoxy systems (page 4) and polyols, for fast-reacting polyurethane systems to produce golf ball components. The invention record further describes that suitable chemical compositions for RIM processing are those that have a relatively quick gel time, *e.g.*, 0.25 to 5 seconds (page 5). However, the viscosity for components A and B can be increased to 3,500 cps with a gel time extended to 10 seconds (page 5). Certain information has been redacted in accordance with standard practice. However, all redacted dates are prior to October 1, 1999.

6. That we have reviewed the document of Exhibit A. Although the dates of Exhibit A have been blanked out, the dates are all prior to October 1, 1999. We hereby confirm that the work evidenced by the document of Exhibit A and all the acts relied upon in this Declaration were carried out by us or someone acting at our direction in the United States prior to October 1, 1999.

7. That the document of Exhibit A is the same as the invention record previously submitted in the Declaration of Manjari Kuntimaddi executed on July 18, 2005, submitted August 8, 2005, and resubmitted on February 2, 2006. After having reviewed the Examiner's comments in a Final Office Action mailed June 15, 2006 regarding "evidence missing . . . due to the pages not sequentially making sense," however, further investigation revealed the proper sequence of pages of the document, now submitted herewith.

8. That attached hereto is Exhibit B. Exhibit B includes a copy of an e-mail documenting plans for a trip to Bayer where the testing shown in the invention record of Exhibit A was performed under a Confidentiality Agreement. This exhibit also includes a copy of the trip summary. This trip summary describes the work done by Bayer at the request of the inventors. For example, the process, materials, molding parameters, and ball construction details are discussed in the trip summary. Certain information has been redacted in accordance with standard practice. However, all redacted dates are prior to October 1, 1999.

9. That we have reviewed the document of Exhibit B. We hereby confirm that the work evidenced by the document of Exhibit B and all the acts relied upon in this Declaration were carried out by us or someone acting at our direction in the United States prior to October 1, 1999.

We further declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted,

Date: 11/23/2006

Shenshen WU

Date: _____

Murali RAJAGOPALAN

Date: _____

Manjari KUNTIMADDI

Date: _____

Kevin M. HARRIS

8. That attached hereto is Exhibit B. Exhibit B includes a copy of an e-mail documenting plans for a trip to Bayer where the testing shown in the invention record of Exhibit A was performed under a Confidentiality Agreement. This exhibit also includes a copy of the trip summary. This trip summary describes the work done by Bayer at the request of the inventors. For example, the process, materials, molding parameters, and ball construction details are discussed in the trip summary. Certain information has been redacted in accordance with standard practice. However, all redacted dates are prior to October 1, 1999.

9. That we have reviewed the document of Exhibit B. We hereby confirm that the work evidenced by the document of Exhibit B and all the acts relied upon in this Declaration were carried out by us or someone acting at our direction in the United States prior to October 1, 1999.

We further declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted,

Date: _____

_____

Shenshen WU

Date: 11/21/06

M. Rajan

Murali RAJAGOPALAN

Date: 11/21/06

K. Rajan

Manjari KUNTIMADDI

Date: 11-22-06

Kevin M. HARRIS

Case Number TFJ00-031

INVENTION RECORD

1. Short, descriptive title of the invention

Reaction Injection Moldable Chemical Compositions and Method for Making the Same

2. Inventors

a.) Last Name, First Name, Middle Initial
Wu, Shenshen

Street Address, City, State, Zip
334 Old Westport Road, North Dartmouth, MA 02747

Citizen of Country
USA

b.) Last Name, First Name, Middle Initial
Rajagopalan, Murali

Street Address, City, State, Zip
11 Flagship Drive, South Dartmouth, MA 02748

Citizen of Country
USA

c.) Last Name, First Name, Middle Initial

Kuntimaddi, Manjari
1261 Church Street, # 13
New Bedford, MA 02745
Citizen of India

d.) Last Name, First Name, Middle Initial

Harris, Kevin
65 Ryan Street, New Bedford, MA 02740
Citizen of USA

3. What do you think the invention is?
(Describe in a few sentences what is novel about your invention)

The invention discloses a faster, potentially cheaper way to make polyurethane components or other reactive materials for golf balls, including covers, cores, and inner layers. This invention also expands on the potential, previously undisclosed materials available for golf ball manufacturing.

Commercially available polyurethane covered golf balls that are currently sold in the market are processed either by the castable urethane process or by the injection molding process when the thermoplastic polyurethane (TPU) material is used. When the castable process is used, the reaction time generally is slow. It greatly restricts the utility of other useful chemical

compositions that are faster reacting in nature. The present invention addresses this deficiency by utilizing a Reaction Injection Molding (RIM) process.

4. **How does it work?**
(Please provide a detailed description of the invention. You can use sketches, drawings, flow sheets, chemical equations, etc. to help understanding by others.)

In the RIM process, at least two or more reactive low viscosity liquid components are mixed by impingement and injected under high pressure (1200 psi or higher) into an open or a closed mold. The reaction times for the RIM systems are much faster than the low pressure mixing and metering machines, consequently, the raw materials used for the RIM process are generally much lower in viscosity to allow intimate mixing by impingement in a very short time.

The use of additives such as colorants, processing aid, foaming agents, and fillers is also applicable.

A schematic representation of a typical RIM process is shown in (Figure 1) enclosed.

5. Are there any other uses for your invention?
(This answer will help to get the broadest possible patent protection and identify other areas where there may be relevant prior art)

The RIM process can be used to mold centers, mantles, covers, shoe soles, club shafts, iron/ putter inserts and club heads; and other areas, such as integral skin foam, high modulus and low modulus elastomers, and rigid structural foam systems.

High modulus elastomeric systems typically are formulated to a 1.0 – 1.1 specific gravity and a material Shore hardness of 60 – 75 D. Flexural modulus ranges between 25,000 – 130,000 psi. Typical applications for high modulus elastomers are bumper covers, business machine housings, urethane/filler composites, rigid structural foams for electronic cabinetry, and body panel parts of all types.

Low modulus elastomeric systems have a material Shore hardness of less than 60 D and a flexural modulus of lower than 25,000 psi. Typically applications for low modulus elastomers are flexible urethane gaskets, carpet under lays, energy absorbing foams, and integral skin foams that provide soft, aesthetic surfaces.

6. **What is new about your invention and how does it improve on the present situation?**
(You might wish to answer one or more of the following questions: What are the technical problems it will solve? What are the commercial problems it will solve?)

- Commercially available polyurethane covered golf balls that are currently sold in the market are processed either by the castable urethane process or by the injection molding process when the thermoplastic polyurethane (TPU) material is used. When the castable process is used, the reaction time generally is slow. It greatly restricts the utility of other useful chemical compositions that are faster reacting in nature. The injection moldable thermoplastic polyurethane (TPU) limits to only those elastomers that are thermoplastic in nature. The present invention addresses these deficiencies by utilizing a Reaction Injection Molding (RIM) process.

- RIM process differs from the castable urethane process in that the raw materials used in the RIM process are faster reacting and lower in viscosity. RIM machine can process fast reacting materials having viscosity up to about 2,000 cps and a pot life of less than five seconds. Because of the low viscosity materials used in the RIM process, Components A & B and possibly a third and a fourth stream are capable of being mixed

by impingement in less than a second before injecting the mixed material into the closed mold at about 2,000 – 2,500 psi. Whereas, the conventional castable urethane process normally is capable of handling raw materials having processing viscosity up to 3,500 cps and a pot life of more than 35 seconds. Because of the slower reacting and higher viscosity raw materials used, the castable process employs mechanical mixing and requires a much longer mixing time.

- Various resilient and durable castable urethane formulations that are too fast for the conventional castable urethane method can be processed with the present invention. Faster reaction rate will eventually translates into increased productivity after the process is optimized.

- The RIM process is also suitable for molding layers as thin as 0.020" or less, which is difficult – if not impossible – with other molding methods.

- Material costs for RIM materials are potentially much lower than with castable materials.

7. Do you know of any published literature relevant to your invention? What concept(s) that you have found appears closest to your invention...and how is your invention different? Where have you looked and what did you find? If you have not yet looked, do so now. Do not proceed without at least a search of US Patents in the last 20 years. A searchable database is available online and we have copies of all golf patents in house.

("Literature" includes other patents, patent applications, published papers, conference proceedings, trade literature, magazine articles, etc.)

PMA RIM Design Conference proceeding on **Reaction Injection Molding of Light Stable Polyurethane Systems** by Colorim Systems, October, 1985.

PMA RIM Design Conference proceeding on **What is RIM?** by Krauss Maffei Corporation, October, 1985.

PMA RIM Design Conference proceeding on **Innovation in RIM Polyurethane Markets** by Mobay Chemical Corporation, October, 1985.

Teltech literature search prepared for Shenshen Wu dated October 4, 1999.
Teltech literature search prepared for Shenshen Wu dated October 5, 1999.
Teltech literature search prepared for Manjari Kuntimaddi dated September 26, 2000.

Issued US Patent # 6,083,119 on July 4, 2000 by Spalding Sports Worldwide, Inc. on **Multi-Layer Golf Ball.**

— requires additional review —

PMA Conference proceeding on **Reaction Injection Molding (RIM) Tchnology – New Horizens** by Bayer Corporation, October 3rd, 2000.

8. When and where was the idea of the invention first conceived? Who participated? (It is important to note whether the invention was made in collaboration with people - including vendors and consultants - in other departments or even other companies. Focus on "Inventor" – the person(s) who thought up or imagined or produced the invention for the first time through the use of imagination or ingenious thinking and experimentation. You should not list "implementers" who simply take the inventor's instructions and fabricate something.)

The idea of the invention was first conceived on as evidenced by Murali Rajagopalan's e-mail message to Kevin Harris dated The conception took place in by K. Harris and S. Wu during the experimental development of the Titleist Professional. No documentation of this fact is available at this writing...but we'll keep looking. (see also the attached Memorandum from Kevin Harris to Bill Morgan.)

9. When did you make the first notes or sketches? Where?

Please see the explanations described above.

10. Has your invention only been demonstrated in your laboratory, or has it been used outside (ex: Pilot Run in the plant or a trial at another manufacturing facility)? Summarize the results that best demonstrate your invention ("Best mode"). Please identify where the results are recorded.

(You may attach copies of formal project reports if this is more convenient. Test results provide evidence that the invention works and provides the intended result)

A reduction to practice of the invention was made at Bayer's lab under "Work For Hire" agreement during the week of The core used for this trial is the HP Distance 1.390" core. The mantle formulation is Bayflex 110-35 IMR system; and the cover formulation is Bayflex XGT-80. Physical properties of each component is tabulated below.

Component Properties	Core	Mantle	Finished Ball
Size, (inches) Pole Equator	 1.390 1.390	 1.510 1.510	 1.676 1.684
Weight, oz (g)	0.952 (27.0)	1.186 (33.6)	1.616 (45.8)
Corr. Compression	50	69	110
COR @ 125 ft/sec	0.776	0.754	0.745
Material Hardness Shore D		35	65
Core Surface Hardness, Shore D	45.2		

Other suitable formulations for the RIM process include:

a. Low %NCO MDI/polybutadiene diol prepolymer cured with Unilink 4200.
b. Aromatic and/or aliphatic prepolymers cured with fast reacting aromatic and/or aliphatic diamines.
c. Quasi-prepolymers cured with polyol/diamine curative blends.
d. Quasi-prepolymers cured with polyols with catalyst.
e. Fast reacting polyurea systems.
f. Fast reacting coating systems, solvent and/or solventless.
g. Interpenetrating Polymer Networks with

1. Polyurea/polyurethane (using aliphatic and/or aromatic systems) and polyacrylic systems.
2. Polyurethane/polyurea/epoxy systems. For example, MDI prepolymer/DER 331 cured with Jeffamines.

In some cases, the following treatments were also made to the cores prior to mantle molding when the adhesion of the core to the mantle layer was inferior.

a. Corona and/or Plasma treat the core surface.
b. Flame treat the core surface.

c. Apply adhesion promoters to the core surface, such as Eastman 343-1 & 3, Eastman 515-2, Bayer 8713, Bayer U42 & U53, Bayer 140AQ, Ricobond, and Witcobond.

The present invention comprises RIM chemical compositions having at least 5% NCO (isocyanate) concentration in the prepolymer and/or quasi prepolymer, and a component A to Component B ratio range of 0.02 : 1 to 10 : 1.

Suitable materials for use in Component A include pure isocyanates, quasi-prepolymers; and prepolymers having a viscosity range from 25 cps to 2,000 cps processable at either ambient temperature and/or at an elevated temperature.

Suitable curing agents for Component B include polyols and polyamines having functionality of at least two; and having a viscosity range from 25 cps to 2,000 cps processable at either ambient temperature and/or at an elevated temperature.

Suitable chemical compositions for process by RIM are those chemical formulations, with or without a catalyst, that having a gel time ranging from ⅛ second to 5 seconds.

When an internal mixer is used, the upper limit viscosity of Components A & B can be increased to 3,500 cps with a gel time extended to 10 seconds.

These chemical compositions can optionally be foamed using either chemical blowing agents such as water or non-reactive gases like Freon, nitrogen, helium, etc. The micro-cellular foam process can be used in the present invention.

The density of these chemical compositions can further be adjusted by the addition of fillers such as metallic powders, metal oxides, and other metal derivatives.

Suitable catalysts for use in the RIM process include fast reacting aromatic and aliphatic amines such as Ethacure 100, Clearlink 1000 & 3000, Jeffamines, isophorone diamine, 1,3- and 1,4-diaminocyclohexane, 1,3- and 1,4-cyclohexane bis(methylamine), 4,4'-dicyclohexylmethane diamine, diethylene glycol di-(aminopropyl)ether, 5-amino-1,3,3-trimethyl-cyclohexane-methylamine, etc.; tin catalysts such as dibutyltin dilaurate; amine catalysts such as triethylenediamine; organic acids such as acetic acid or oleic acid; and delayed catalysts such as POLYCAT SA-1, SA-102, SA-610/50, etc. manufactured by Air Products and Chemicals, Inc. Suitable catalyst concentrations in the elastomers ranges from about 0.001% to about 3.0%

Suitable isocyanates include, but not limited to, 4,4'-diphenylmethane diisocyanate (MDI); polymeric 4,4'-diphenylmethane diisocyanate (polymeric MDI); carbodiimide modified 4,4'-diphenylmethane diisocyanate (liquid MDI); toluene diisocyanate (TDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI); para-phenylene diisocyanate (PPDI); xylylene diisocyanate (XDI); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene diisocyanate (HDI); 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl cyclohexylene diisocyanate; meta-tetramethylxylene diisocyanate (*m*-TMXDI); para-tetramethylxylene diisocyanate (*p*-TMXDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI); isophorone diisocyanate (IPDI); cyclohexyl diisocyanate (CHDI); 1,5-naphthalene diisocyanate (NDI); trimerized isocyanurate of TDI; isocyanurate of toluene diisocyanate; isocyanaurate of hexamethylene diisocyanate; dimerized uretdiones of TDI; etc., and mixtures thereof.

Suitable polyols include, not not limited to, polyether polyols such as polytetramethylene ether glycol; poly(oxypropylene) glycol; and poly(ethylene oxide capped oxypropylene) glycol. Suitable polyester polyols include polyethylene adipate glycol; polyethylene propylene adipate glycol, polybutylene adipate glycol; polycarbonate glycol. Suitable polycaprolactone

polyols which are useful in the present invention include diethylene glycol initiated polycaprolactone, 1,4-butanediol initiated polycaprolactone, 1,6-hexanediol initiated polycaprolactone; neopentyl glycol initiated polycaprolactone; and polytetramethylene ether glycol initiated polycaprolactone; hydroxylated acrylic polyols; Bisphenol A based epoxies; castor oils. Copolymers and mixtures of these polyols are also suitable. These polyols have a average molecular weight of about 200 to 4000.

Suitable hydroxy-terminated curing agents include, but not limited to, ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; dipropylene glycol; polypropylene glycol; 1,3-butanediol; 1,4-butanediol, 2,3-butanediol; 2,3-dimethyl-2,3-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(beta-hydroxyethyl) ether and its derivatives; hydroquinone-di-(beta-hydroxyethyl) ether and its derivatives; 1,3-bis-(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy} benzene; 1,3-bis-(2-hydroxyethoxy) cyclohexane; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] cyclohexane; 1,3-bis-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy} cyclohexane; 2-propanol-1,1'-phenylaminobis; trimethylolpropane; polytetramethylene ether glycol having molecular weight from 250 to 3900; and mixtures thereof.

The molecular weight of the diols is at least 50.

Suitable amine-terminated curing agents include, but not limited to, tetrahydroxypropylene ethylene diamine; 4,4'-methylenebis-(2-chloroaniline); 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; 3,5-diethyltoluene-2,4-diamine; 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene; 1,2-bis-(sec-butylamino)-benzene; derivatives of 4,4'-bis-(sec-butylamino)-diphenylmethane; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,4-bis-(sec-butylamino)-cyclohexane; 1,2-bis-(sec-butylamino)-cyclohexane; derivatives of 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; N,N'-dialkylamino-diphenylmethane; trimethyleneglycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-methylene-bis-(2-chloroaniline); meta-phenylenediamine; para-phenylenediamine; 4,4'-dicyclohexylmethane diamine; cyclohexyldimethylol; 1,4-cyclohexane-bis-(methylamine); 1,3-cyclohexane-bis-(methylamine); diethylene glycol di-(aminopropyl) ether; 2-methylpentamethylene-diamine; diaminocyclohexane; triisopropanolamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; propylene diamine; 1,3-diaminopropane; dimethylamino propylamine; diethylamino propylamine; imido-bis-propylamine; diethanolamine; triethanolamine; diisopropanolamine; isophoronediamine; and mixtures thereof.

The amine curing agent has a molecular weight of about 64 to 2000.

11. Has the invention been disclosed outside the company? yes

- If yes, was a non-disclosure agreement signed? yes
- Please give date of the event: During the week of
- Describe event

During the week of , a trip was made to Bayer Corporation in Pittsburgh. We explored the RIM process for fast reacting polyurethane systems to produce golf ball mantles and covers. Bayer made a prototype mold using our golf ball dimple cavities and custom-made mantle cavities with fixed pins for feasibility study under our supervision. The mantle and cover formulations were provided by Bayer at this trial.

Several mantles and golf balls were molded during this trip.

12. Signature of Inventor(s)
(You must have two witnesses - one of which must be director level or above. Each witness must have read and understood the invention record.)

Inventors

a.) Shenshen Wu
b.) Murali Rajagopalan
c.) Manjari Kuntimaddi
d.) Kevin Harris

Witness#1

Address
14 Sleepy Hollow Rd
Dartmouth, MA 02747

Witness#2

Address

Shenshen Wu
12:10 PM

To: Murali Rajagopalan@TFJWW
cc: Kevin Harris@TFJWW, Manjari Kuntimaddi@TFJWW
Subject: Re: Bayer RIM trial (Document link: Manjari Kuntimaddi)

I can make it on

Murali Rajagopalan

To: Kevin Harris@TFJWW, ShenShen Wu@TFJWW, Manjari Kuntimaddi@TFJWW
cc: Derek Ladd@TFJWW, Scott Barber@TFJWW
Subject: Bayer RIM trial

Kevin, Shenshen, Manjari:

Harry George from Bayer returned my call today and suggested us to come over on so that we can run the RIM trail on (. Could you please check with your calendar and advise me today so that I will inform Harry accordingly. Harry told me that he will make hotel arrangements for our stay on Monday evening.

We will send fresh cores of 1.39" for mantle/ball molding work next week .... we will advise them to use Bayflex 110-35 MR as a mantle material (so we can compare against our Hytrel mantle) and use Bayflex 110-50 MR (58 D) or 110-80 (67 D) as a cover material.

Bayer will be conducting this trial in their R&D equipment at their Pittsburgh R&D facility and he might be able to take a tour of other buildings like polymer processing/testing etc.. as time permits.

Thanks.

Murali

Murali Rajagopalan

To: Manjari Kuntimaddi@TFJWW, ShenShen Wu@TFJWW
cc:
Subject: Re:Bayer (Document link: Manjari Kuntimaddi)

Manjari and Shenshen:

Please find attached a document with minor corrections.. it looks pretty good... if Shenshen does not have anything to add then it is ready to for distribution!!

Thanks.

Murali

(See attached file: Bayertripdraf2.doc)

TITLEIST AND FOOT-JOY WORLDWIDE
INTER-OFFICE CORRESPONDENCE

To: **Kevin Harris**
From: **Shenshen Wu, Manjari Kuntimaddi and Murali Rajagopalan**
Subject: **Bayer Trip Report –Reaction Injection Molding of Golf Ball Covers/Mantles**

People Attended:

Titleist:
Shenshen Wu, Manjari Kuntimaddi and Murali Rajagopalan

Bayer (RIM Polyurethane group)

Harry M. George – Senior Technical Marketing Specialist
Stephen J. Harasin – Technical manager
Matthew R. Nagy – Design Engineer

SUMMARY

During our visit to Bayer Corporation in Pittsburgh, we explored a relatively new process to the golf industry called the Reaction Injection Molding (**RIM**) process for fast reacting polyurethane systems to produce golf ball covers and mantle layers. Bayer made a protocol mold using our golf ball dimple cavities and custom-made mantle cavities with fixed pins for feasibility study.

The mantles molded at Bayer prior to our visit had severe "delamination" (i.e. void) between the mantle and a core layer due to poor adhesion. During the trial, we were able to eliminate this to a great extent by surface modifying the cores either by using flame treatment or by dipping in functional polymer emulsion. Adhesion characteristics of these surface treated cores will be evaluated and the best surface treated candidate will be selected for further research towards the golf ball.

However, we found excellent adhesion between the outer RIM based polyurethane hard cover (67 Shore D) and an inner RIM based polyurethane soft cover (35 Shore D). Golf balls having a RIM based outer and inner polyurethane cover layers exhibited excellent adhesion in comparison to our existing multi-layer balls.

We strongly recommend to bring the RIM process in-house in the immediate future since this process has several potential benefits when compared to the existing casting urethane process such as:

- short cycle time of 45 seconds or less.
- thinner cross-section of 0.020" is feasible.
- could be a relatively less expensive process based on the raw materials.
- could be used as a relatively low temperature process which will allow direct injection molding over wound balls.
- Potential patent opportunities which need to be pursued vigorously to be ahead of the competition.
- In addition, we can also evaluate some of our own proprietary fast reacting formulations, which cannot be processed in the existing castable process.

Background:

About two years ago, shortly after the show in Chicago, Titleist approached Harry George, Senior Technical Marketing Specialist for RIM polymers at Bayer, to explore any opportunities using the RIM process for the golf ball application. Due to a slow response from their legal department, it took over a year for both Titleist and Bayer to sign the reciprocal confidentiality agreement in order to proceed with the evaluation of their RIM process for our golf ball application. (See attachment for email communications).

A successful preliminary meeting between Titleist and Bayer in initiated both teams to pursue the RIM process for golf ball application. The following activities followed that meeting:

- Titleist forwarded cover/mantle material property requirements to Bayer in
- Additional meeting in to further define the upcoming RIM trial.
- Bayer initiated a proposal to make a proto-type mold for mantles and covers using fixed pins to minimize initial expenses and faster response for the early molding trial.
- Titleist provided dimpled golf ball cover cavities and purchase order for $4,800 to Bayer towards for mantle/fixed pins/aluminum based prototype mold in
- Titleist sent about 300 cores having 1.39" diameter (HPdistance cores) for Bayer's initial machine set-up and debugging of their RIM process.
- Several RIM based polyurethane mantles having 35 shore D and double cover based on RIM polyurethane outer having 65 shore D and inner cover having 35 shore D were processed by Bayer in
- Titleist, upon Bayer's request, participated in their molding trial, visited their labs and meet with several technical staff in the RIM and Engineering Polymers divisions, during the week of

Bayer Trip/RIM trial Details

The primary purpose of this trip was to:

- Learn about RIM process and investigate its potential feasibility for golf ball application.

- Meet with Hennecke Machinery Division – a fabricator of RIM machines.
- Meet with other engineering polymers group from Thermoplastic Polyurethane (TPU) and Polycarbonate group for any potential "new materials" useful in golf ball application.

(1) How does RIM process differs from our castable polyurethane process?

RIM process differs from the castable urethane process in that the raw materials used in RIM process are faster reacting and lower in viscosity. RIM machine can process fast reacting materials having viscosities up to 1,000 cps and a pot life of less than five seconds. Because of the low viscosity materials used in the RIM process, the prepolymer(s) and the curing agent(s) are capable of being mixed by impingement in less than a few seconds before injecting the mixed material into the mold at about 2,000 psi. For example, a total cycle time in the Bayer trial including the demolding was less than 45 seconds.

On the other hand, the current castable process at Titleist is capable of handling raw materials having processing viscosities up to 3,000 cps and a pot life of up to 80 seconds. Because of the slow reacting and high viscosity raw materials used, the castable process employs mechanical mixing (rotor) and requires a longer mixing time such as 20 seconds.

Machinery and RIM based golf ball mantles and cover constructions used in this trial

RIM Equipment Used:

- Hennecke custom designed mini-RIM machine having dual lance cylinders and 8 mm MQ mixer head.
- Prototype mold was constructed using aluminum base and mantle core cavity (1.510" diameter) and pins were made by stainless steel.
- Single cavity with an outlet for excess material.

RIM Raw Materials Used:

- Component A - Quasi MDI prepolymer – viscosity of about 200 to 300 cps stored at 95F and the piston pressure 2000 psi.
- Component B – a blend of polyol with an amine curative – viscosity of about 200 to 300 cps - stored at 120F to 130F and the piston pressure is 1800 psi.

Molding Parameters:

- Shot-size about 25g – 35g.
- Injection pressure at the injection nozzle was about 2000 psi.
- Mold temperature was 110F to 120 F.

Ball Construction Details:

Mantles:

- Used 1.39" cores (HP distance cores, about 50 atti compression)
- Molded RIM polyurethane having a hardness of about 35 shore D over the 1.39" cores to produce 1.51" mantles.

Ball Cover:

- Used 1.51" mantle from the above and molded RIM polyurethane cover having a hardness of about 65 Shore D to produce golf balls having a diameter of about 1.68".

Hennecke Machinery

We also visited one of the RIM equipment manufacturers associated with Bayer, Hennecke Machinery in Pittsburgh area. We discussed different machinery and their capability. Some of the literature is attached for review. Meanwhile, we are also contacting other RIM machinery suppliers to identify a suitable R&D RIM machine.

Miscellaneous:

Thermoplastic Polyurethane (TPU)

We met with some Texin staff and they briefed us about their existing TPU products including a developmental TPU based on 75A or 70A. We requested the TPU staff to provide with Bashore rebound and flexural modulus data on certain grades so we can decide if any additional work is warranted for our golf ball evaluation.

Polycarbonate

We also met with Polycarbonate staff and learnt about their product lines. Although, the conventional polycarbonates have a very high flexural modulus (over 350 kpsi) which are unsuitable for covers or mantles but appropriately blending with soft elastomers might produce some useful compositions for the golf ball application (Murali has done work in the past and need to follow-up). We can also use high distortion temperature material like polycarbonate in the liquid center non-wound golf balls (Mitch is currently evaluating it).

Conclusion

Based on the visit and the trial, we strongly recommend pursuing the RIM technology in Titleist R&D for golf ball application. It was very encouraging to find the golf balls having a RIM based outer and inner polyurethane cover layers exhibited excellent adhesion in comparison to our existing multi-layered balls.

Action Plan for future work:

(1) Work with several RIM machine manufacturers to identify a suitable -RIM machine for our research work to evaluate our in-house fast reacting urethane formulations for both mantles and covers.

(2) Work with Bayer and other RIM machine manufacturers to further strengthen our understanding about RIM and mold design/materials requirements.

(3) Continue to work with Bayer to mold prototype RIM Polyurethane covers over wound construction for feasibility study.

(4) Explore other avenues for improved adhesion between the core and the mantle layer.